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HYDROGEN SULFIDE

[7783-06-4]

Formula: H_2S ; MW 34.08

Synonyms: sulfur hydride; sulfureted hydrogen

Occurrence and Uses

Hydrogen sulfide occurs in natural gas. It also is found in many sewer gases. It is a by-product of many industrial processes. Trace amounts of dissolved H_2S are found in wastewaters in equilibrium with dissolved sulfides and hydrosulfides. It also is found in volcanic eruptions, hot springs and in troposphere. The average concentration of H_2S in the air is about 0.05 ppb.

The most important applications of hydrogen sulfide involve the production of sodium sulfide and other inorganic sulfides. Hydrogen sulfide obtained as a by-product often is converted into sulfuric acid. It also is used in organic synthesis to make thiols or mercaptans. Other applications are in metallurgy for extracting nickel, copper, and cobalt as sulfides from their minerals; and in classical qualitative analytical methods for precipitation of many metals (see Reactions). It also is used in producing heavy water for nuclear reactors.

Physical Properties

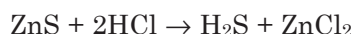
Colorless gas; characteristic odor of rotten eggs; odor threshold 1ppm; sweetish taste; fumes in air; flammable gas, burns with a pale blue flame; refractive index at 589.3nm, 1.000644 at 0°C and 1 atm; density 1.539 g/L at 0°C; critical temperature 100.4°C; critical pressure 88.9 atm; liquefies at -60.7°C; solidifies at -85.5°C; velocity of sound 289 m/sec in H_2S gas; slightly soluble in water (0.4% at 20°C); pH of a saturated aqueous solution 4.5; slightly acidic; diffusivity in water at 16°C, $1.77 \times 10^5 \text{ cm}^2/\text{sec}$; soluble in carbon disulfide, methanol, acetone; very soluble in N-methylpyrrolidinone and alkanolamines (salt formation occurs: salt dissociates on heating); liquid H_2S dissolves sulfur and SO_2 .

Thermochemical Properties

ΔH_f°	-4.93 kcal/mol
ΔG°	-8.02 kcal/mol
S°	49.16 cal/degree mol
C_p	8.18 cal/degree mol
Thermal conductivity (15°C)	$33.3 \times 10^{-6} \text{ cal/sec.cm}^2.\text{°C/cm}$

Production

Hydrogen sulfide may be prepared conveniently in the laboratory in a Kipp apparatus by the reaction of iron(II) sulfide or zinc sulfide with dilute hydrochloric or sulfuric acid:

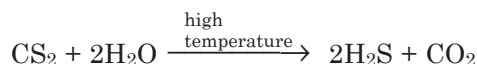
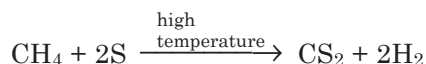


A steady supply of hydrogen sulfide may be maintained by adding acid from

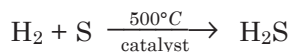
time to time.

H₂S is produced in large scale by several processes, which are:

1. Refining crude oil by hydrodesulfurization. The crude oil contains varying amounts of sulfur that may range from 0.05 to about 5%. The sulfur-rich fractions, the coke-distillate and the gas-oil fractions of the crude oil are passed through a fixed-bed catalyst along with hydrogen.
2. It also is produced as a by-product by hydrodesulfurization of coal or liquefaction of coal.
3. It also is obtained by the reaction of methane with sulfur vapor to produce carbon disulfide which on hydrolysis yields H₂S:



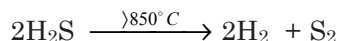
4. Heating hydrogen and sulfur vapor at 500°C in the presence of a catalyst, such as, bauxite or cobalt molybdate, which produces a high purity H₂S:



Reactions

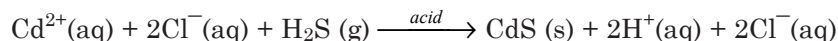
There are four types of H₂S reactions: decomposition, precipitation, oxidation, and organic addition.

Thermal dissociation of H₂S is rapid above 850°C, producing hydrogen and sulfur. The reaction is endothermic.

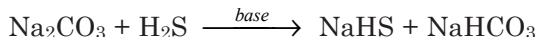
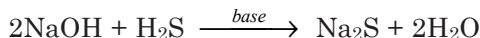
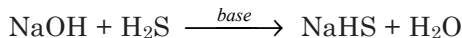


The dissociation also is rapid below this temperature (between 450°C to 850°C), however, only in the presence of a catalyst, such as silica, platinum sulfide or cobalt molybdate. Other sulfur species are also produced in the reaction.

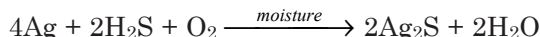
Hydrogen sulfide forms precipitates of several metal sulfides when passed through an aqueous solution of metal salts. Under acid conditions, several metals including arsenic, antimony, bismuth, cadmium, copper, lead, mercury, and tin are precipitated as their sulfide; e.g.;



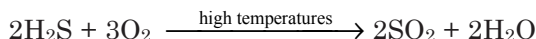
Under ammoniacal conditions, iron, cobalt, nickel, zinc and manganese precipitate as sulfides.



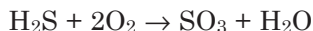
In the presence of moisture at ordinary temperatures, H_2S reacts with some metals, such as copper and silver, forming sulfides:



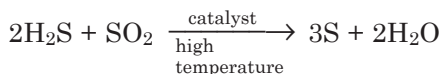
Hydrogen sulfide undergoes thermal or catalytic oxidation with oxidizing agents forming sulfur, sulfur oxides, or sulfur derivatives. The products formed depend on reaction conditions and the nature of oxidizing agents. Combustion in air in the presence of flame primarily produces sulfur dioxide:



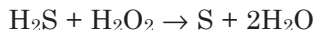
Sulfur trioxide is a minor product in such oxidation:



When a mixture of H_2S and SO_2 gases are passed over a catalyst such as silica gel at elevated temperatures, sulfur and water are formed:

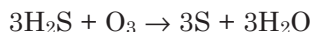


Stronger oxidizing agents such as hydrogen peroxide or ozone readily oxidize H_2S forming sulfur and various other sulfur products. For example, H_2O_2 reacts with H_2S under neutral conditions forming sulfur and water:

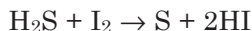


In alkaline solution however, the reactions are more complex and the products include thiosulfate and sulfate.

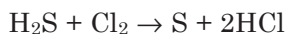
Oxidation with ozone in aqueous conditions yields sulfur and sulfuric acid:



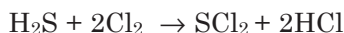
In aqueous solution, H_2S and iodine react to form sulfur and hydriodic acid:



In gaseous phase, chlorine and H_2S react at equimolar ratio, forming sulfur and hydrogen chloride:



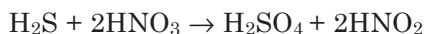
In excess chlorine, the product is sulfur dichloride:



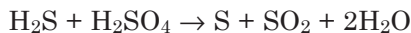
In aqueous solution, however, chlorine in higher molar ratios oxidizes H_2S to sulfuric acid:



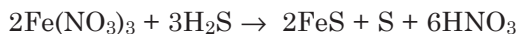
In aqueous solution nitric acid also oxidizes H_2S to sulfuric acid.



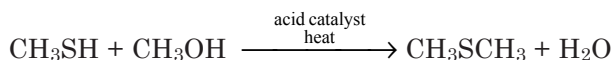
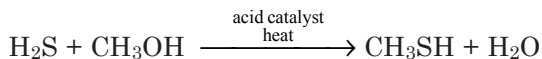
Reaction with concentrated sulfuric acid yields sulfur and sulfur dioxide:



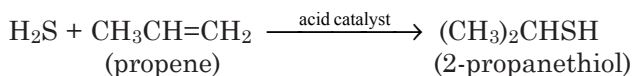
In aqueous solutions, metal ions in their higher oxidation states oxidize H_2S , forming a lower-valence sulfide and sulfur:



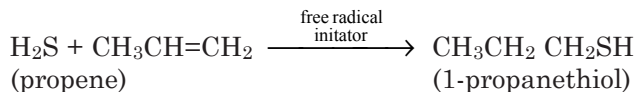
Hydrogen sulfide also reacts with many types of organic substances. Reaction with methanol at high temperatures in the presence of an acidic catalyst yields methanethiol and dimethylsulfide:



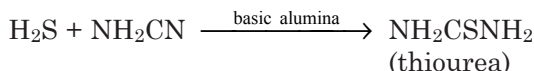
H_2S adds to olefins in the presence of acid catalysts forming thiols (mercaptans):



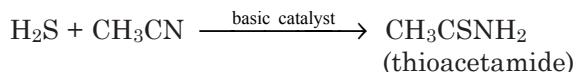
In the presence of a free radical initiator, the product is 1-propanethiol:



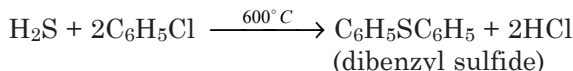
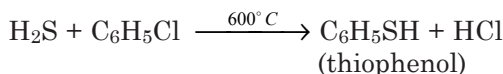
Reaction with cyanamide in the presence of basic catalyst yields thiourea:



Under similar conditions, reactions with nitriles yield thioamides:



Reaction with chlorobenzene at elevated temperatures yields thiophenol as major product and dibenzyl sulfide in smaller amounts:



Analysis

Elemental composition: H 5.92%, S 94.08. Hydrogen sulfide may be distinguished by its characteristic odor. The gas turns a paper soaked in lead acetate solution black. Many infrared sensors are commercially available for *in-situ* measurements of H₂S. It may be monitored semiquantitatively by Draeger tubes. It also may be analyzed by GC following trapping over molecular sieves and thermal desorption. Either a flame photometric detector or a sulfur chemiluminescence detector may be used for GC analysis. It may be separated on a capillary column such as Carboxen 1006 PLOT™ or SPB-1 SULFUR™ (*Supelco Catalog 1999*: Supelco Inc., Bellefonte, PA).

Hazard

Hydrogen sulfide is a highly toxic and flammable gas. A 5-minute exposure to 1,000 ppm concentration in air can be fatal to humans (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley). The symptoms are headache, nausea, nervousness, cough, eye irritation, and insomnia. High doses can produce unconsciousness and respiratory paralysis.

Hydrogen sulfide forms explosive mixtures with air; the LEL and UEL are 4.3 and 45.0% by volume in air, respectively. Its autoignition temperature is 260°C. Its reaction with soda-lime in oxygen can be explosive. Reactions with strong oxidizing agents can progress to incandescence.

HYDROGEN TELLURIDE

[7783-09-7]

Formula: H_2Te ; MW 129.62**Uses**

Hydrogen telluride is used in preparation of telluride salts.

Physical Properties

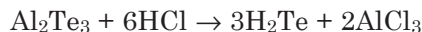
Colorless gas; strong garlic-like odor; stable to light when dry but undergoes photochemical decomposition in the presence of moisture and dust; density 5.68 g/L; liquefies to a colorless unstable liquid at -2°C , decomposed by light; liquid density 2.57 g/mL at -20°C ; solidifies at -49°C ; soluble in water, alcohol and alkalis; pKa 2.6 (for first dissociation constant at 18°C) and 11.0 (the dissociation constant at 25°C) for the second replaceable hydrogen.

Thermochemical Properties

ΔH_f°	23.80 kcal/mol
ΔH_{vap}	4.59 kcal/mol

Preparation

Hydrogen telluride is prepared by the reaction of aluminum telluride, Al_2Te_3 with hydrochloric acid:



It also may be prepared by electrolysis of a 50% sulfuric acid solution using a tellurium cathode.

Analysis

Elemental composition H 1.56%, Te 98.44%. The gas is identified by its physical properties and measured by chemical analysis. Two most confirmatory methods recommended here are (1) GC/MS, the characteristic mass ions should be in the range 126 to 132, and (2) furnace-AA or ICP emission spectroscopic analysis for metallic tellurium. For the AA analysis, hydrogen telluride gas should be passed through water and the solution acidified and analyzed for tellurim. Hydrogen may be measured by the classical combustion method involving oxidation to form water, followed by gravimetry.

Toxicity

Hydrogen telluride is a highly toxic gas and a strong irritant to eyes, nose and upper respiratory tract. Toxic properties are similar to hydrogen selenide. Inhalation can cause damage to lungs, liver and spleen. Short exposure to a high concentration can be lethal.

HYDROXYLAMINE

[7803-49-8]

Formula: H_2NOH ; MW 33.03

Synonym: oxammonium

Uses

Hydroxylamine is used as a reducing agent in many inorganic and organic synthetic reactions. Other applications of this compound include purification of aldehydes and ketones; dehairing of hides; as an antioxidant for fatty acids; to stabilize lower oxidation states of metal ions for analysis; and in photography.

Physical Properties

White crystalline solid; orthogonal plates or needles; unstable; density 1.21 g/cm^3 at 20°C ; melts at 33°C ; vaporizes at 58°C ; very soluble in water, liquid ammonia and lower alcohols; sparingly soluble in most other organic solvents; decomposes in hot water; pK_a 5.94 at 25°C .

Thermochemical Properties

ΔH_f° -27.29 kcal/mol

Preparation

Hydroxylamine is unstable as a free base. It is prepared from hydroxylamine hydrochloride, $\text{NH}_2\text{OH} \cdot \text{HCl}$, which is obtained by electrolytic reduction of ammonium chloride solution. The hydrochloride undergoes alkaline decomposition to hydroxylamine, which is collected by vacuum distillation.

Analysis

Elemental composition: H 9.15%, N 42.41%, O 48.44%. Hydroxylamine may be measured by coulometric titration to a potentiometric end point using a coulometric titration cell. A standard solution of bromine may be used as oxidizer in the redox reaction. (Skoog, D. A., D. M. West, and F. J. Holler. 1992. *Fundamentals of Analytical Chemistry*, 6th ed. pp. 467, Orlando: Saunders College Publishing)

Hazard

Hydroxylamine is a poison by oral, subcutaneous, and intraperitoneal routes, the systemic effect being methemoglobinemia. It also is corrosive to skin and an irritant to eyes and respiratory tract.

Hydroxylamine also is a fire hazard. It may ignite spontaneously when placed on paper, and it explodes when heated in air above 70°C . It ignites or explodes when combined with oxidizing agents or alkali metals.

HYDROXYLAMINE HYDROCHLORIDE

[5470-11-1]

Formula: $\text{H}_2\text{NOH} \cdot \text{HCl}$; MW 69.491

Synonym: oxammonium hydrochloride

Uses

Hydroxylamine hydrochloride is used for controlled reduction reactions. It is used in organic synthesis; as an antioxidant for fatty acids; and in photographic developer solutions.

Physical Properties

Colorless monoclinic crystals; hygroscopic; decomposes slowly in moist air; density 1.67 g/cm^3 at 17°C ; melts at 151°C (decomposes); highly soluble in water ($84\text{g}/100\text{g}$ at 20°C); soluble in lower alcohols and glycols; pH of 0.1 molar solution 3.4.

Preparation

Hydroxylamine hydrochloride is prepared by electrolytic reduction of ammonium chloride.

Analysis

Elemental composition: H 5.80%, N 20.16%, Cl 51.02%, 23.02. The aqueous solution may be measured by coulometric titration (See Hydroxylamine).

Toxicity

Hydroxylamine hydrochloride is moderately toxic by ingestion and subcutaneous and intraperitoneal administration. The oral LD_{50} in mice is in the range 400 to 450 mg/kg.

HYDROXYLAMINE SULFATE

[10039-54-0]

Formula: $(\text{H}_2\text{NOH})_2 \cdot \text{H}_2\text{SO}_4$; MW 164.14

Synonym: oxammonium sulfate

Uses

Most applications of this compound are similar to those of the hydrochloride. It is primarily used as a reducing agent for organic synthesis and chemical analysis. Other uses are to purify aldehydes and ketones; to inhibit oxidation of fatty acids; in dehairing hides; in synthesis of oximes for paints and varnishes; in photographic developer solutions; in rust proofing; and as a catalyst.

Physical Properties

Colorless, crystalline solid; melts at 177°C (decomposes); very soluble in

water; slightly soluble in alcohol.

Preparation

Hydroxylamine sulfate may be prepared by mixing stoichiometric amounts of hydroxylamine and sulfuric acid. It also may be prepared by electrolytically reducing an aqueous solution of ammonium sulfate.

Analysis

Elemental composition: H 4.92%, N 17.06%, O 58.49%, S 19.59%. The concentration of hydroxylamine sulfate in aqueous solution may be measured by coulometric titration against a standard solution of oxidizing agent, such as bromine (See Hydroxylamine). Sulfate anion may be measured by ion chromatography.

HYPOCHLOROUS ACID

[7790-92-3]

Formula: HOCl; MW 52.460

Hypochlorous acid exists only in dilute aqueous solution. It is found in many wastewaters that have been subjected to chlorination.

Uses

Hypochlorous acid is used in bleaching fibers and textiles; as an antiseptic; and as a disinfectant for purification. It also is used as a chlorinating agent for aliphatic and aromatic hydrocarbons.

Physical Properties

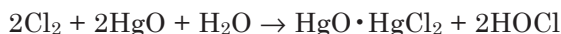
Greenish-yellow aqueous solution; unstable; weak acid, pK_a 7.40 at 25°C; soluble in water.

Thermochemical Properties

ΔH_f° (gas)	-18.81 kcal/mol
ΔG_f° (gas)	-15.80 kcal/mol
S° (gas)	56.57 cal/degree mol
C_p (gas)	8.89 cal/degree mol

Preparation

Hypochlorous acid is obtained by dissolving chlorine in water, or by adding bleaching powder or sodium hypochlorite to water. A better method of production is passing chlorine gas into a well-agitated suspension of mercuric oxide:



or by distilling chlorine hexahydrate and mercuric oxide at low pressure:



The latter process can yield a 25% acid solution.

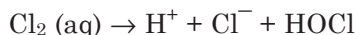
Hypochlorous acid also may be obtained by hydrolysis of chlorine monofluoride:



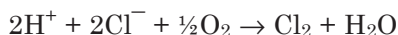
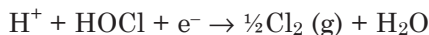
The above reaction may be explosive and is not recommended for preparing hypochlorous acid.

Reactions

Chlorine gas is slightly soluble in water (~6.45 g/L or 0.091 mol/L at 25°C). A disproportion reaction occurs rapidly in water forming hypochlorous acid:



The equilibrium constant, K , for this reaction at 25°C is 4.2×10^{-4} . The standard redox potentials for the following two reactions:



are 1.63V and -0.13V, respectively. A saturated solution of chlorine at 25°C consists of about 33% hypochlorous acid.

The acid is unstable in water. It reacts with hypochlorite ion forming chlorate:



Hypochlorous acid is a strong oxidizing agent which can oxidize many reducing agents, particularly in acid solution. The reaction can be vigorous to violent, depending on reaction temperature and nature of the oxidants.

Analysis

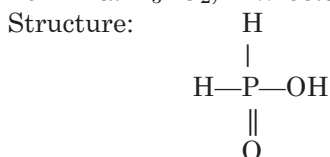
The total free chlorine in wastewaters as measured by colorimetric techniques constitutes both the dissolved molecular chlorine, hypochlorite ion, OCl^- , and hypochlorous acid. An equilibrium exists between these species, the concentrations of which depend on the temperature and pH of the wastewater. Concentration of the hypochlorous acid may be estimated from the K value or from the ratio (33% of the measured concentration of "free" chlorine). The "free" chlorine may be measured by amperometric titration after the addition of a phosphate buffer solution to produce a pH between 6.5 and 7.5. The sample is titrated against a standard solution of phenylarsine oxide. Alternatively, the syringaldazine (3,5-dimethoxy-4-hydroxybenzaldazine) colorimetric test may be performed. This color-forming reagent in 2-propanol yields a colored product with "free" chlorine, the absorbance of which may be

measured by a spectrophotometer at 530nm (APHA, AWWA, WEF, 1999. *Standard methods for the Examination of Water and Wastewaters*, Washington DC: American Public Health Association).

HYPOPHOSPHOROUS ACID

[6303-21-5]

Formula: H_3PO_2 ; MW 65.997



Synonym: phosphinic acid

Uses

Hypophosphorous acid is used to prepare hypophosphite salts and in electroplating baths.

Physical Properties

Colorless deliquescent crystals or oily liquid; sour odor; density 1.493 g/cm³; melts at 26.5°C; boils at 130°C; very soluble in water, alcohol and ether; density of a 50% aqueous solution is 1.13 g/mL.

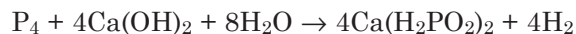
Thermochemical Properties

ΔH_f° (cry)	-144.50 kcal/mol
ΔH_f° (liq)	-142.30 kcal/mol
ΔH_{fus}	2.32 kcal/mol

Preparation

Hypophosphorous acid may be prepared by various methods:

1. Boiling white phosphorus with calcium hydroxide:



The calcium salt is soluble in water. Treatment with sulfuric acid yields the hypophosphorous acid:



The product mixture is filtered to remove insoluble CaSO_4 . The aqueous solution of hypophosphorous acid is concentrated under reduced pressure. Concentrated baryta water may be used instead of calcium hydroxide.

2. By treating sodium hypophosphite, NaH_2PO_2 with an ion-exchange resin. The sodium salt may be produced by boiling white phosphorus with a solution of sodium hydroxide, a reaction similar to (1) above.

3. By oxidation of phosphine with an aqueous iodine solution:

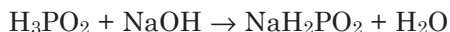


The above method may be considered safer than that involving heating white phosphorus with an alkali.

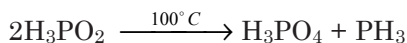
Hypophosphorous acid must be stored below 50°C. It is sold commercially as an aqueous solution at various concentrations.

Reactions

Pure hypophosphorous acid is a monobasic acid, $\text{pK}_a=1.2$. It reacts with bases forming the corresponding salts:



It decomposes rapidly on heating above 100°C to orthophosphoric acid and phosphine:



The phosphorus atom in hypophosphorus acid is in the lowest oxidation state, +1. The compound is, therefore, a powerful reducing agent. It combines readily and often explosively with oxidizing agents. For example, the acid reduces mercury(II) nitrate or mercury(II) oxide into mercury metal violently.

Analysis

Elemental composition: H 4.58%, P 46.94%, O 48.49%. The hypophosphite ion may be oxidized to orthophosphate by careful oxidation. The orthophosphate, PO_4^{3-} ion, may be measured by colorimetry either by using ammonium molybdate and vanadium (yellow color), ammonium molybdate and stannous chloride (blue color), or ammonium molybdate, potassium antimonyl tartrate and ascorbic acid (an intense blue color). Absorbances of the solution are read at 400 (or 470), 650 (or 690) and 880 nm, respectively. Hypophosphite ion alternatively may be identified by ion chromatography.

Hazard

The compound is a very powerful reducing agent. Reactions with oxidizing agents may progress to explosive violence (See Reactions). Also, heating this compound above 100°C can produce toxic phosphine, which also may explode in air.

INDIUM

[7440-74-6]

Symbol In; atomic number 49; atomic weight 114.82; a Group IIIA (Group 13) metallic element; electron configuration $[\text{Kr}]4\text{d}^{10}5\text{s}^25\text{p}^1$; most common valence state: +3; also exhibits valence +2 and +1; two stable isotopes, In-113 (4.23%),

In-115 (95.77%)

History, Occurrence, and Uses

Indium was discovered by Reich and Richter in 1863 in Germany during spectroscopic observations of local zinc ores. The new element was named indium after its characteristic indigo blue spectral lines. Although widely distributed in nature, its concentration is very low, estimated to be about 0.1 mg/kg in the earth's crust. It is found mostly in zinc sulfide ores and to a lesser extent in sulfide ores of iron and copper. The metal does not occur in free elemental form in nature.

A major use of indium metal is in production of bearings for automobile and aircraft engines. Addition of indium improves strength and hardness of bearings and their resistance to corrosion and fatigue. Electroplated coatings of indium are applied onto aluminum for electrical wiring and as indium oxide coatings in sodium-vapor lamps. In the semiconductor industry, In is used as a doping agent to obtain p-type germanium. Other applications are in glass-to-metal seals; in electro luminescent panels; as conductive coatings on glasses and ceramics; and in nuclear reactor control rods.

Physical Properties

Silver-white lustrous soft metal; highly malleable and ductile; face-centered tetragonal crystalline structure ($a=4.583\text{\AA}$, $c=4.936\text{\AA}$); diamagnetic metal; density 7.31 g/cm^3 at 20°C ; melts at 156.6°C ; vaporizes at $2,072^\circ\text{C}$; electrical resistivity $8.4 \times 10^{-6}\text{ ohm-cm}$; superconducting at 3.38°K (-269.8°C); hardness 0.9 (Brinell); tensile strength 26.19 atm; modulus of elasticity 10.8 GPa; thermal neutron absorption cross-section 190 ± 10 barns; soluble in acids.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	58.15 kcal/mol
ΔG_f° (gas)	49.88 kcal/mol
S° (gas)	41.54 cal/degree mol
C_p (gas)	4.97 cal/degree mol
ΔH_{fus}	0.784 kcal/mol
ΔH_{vap}	13.28 kcal/mol
Coeff. linear expansion (at 0 to 100°C)	$25 \times 10^{-6}/^\circ\text{C}$
Thermal conductivity	71.1 W/m.K

Production

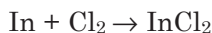
Indium may be recovered from zinc ores by several patented processes. Usually it is recovered from residues obtained from zinc extraction. The residues, slags, fume, or dusts from zinc smelting or lead-zinc smelting are treated with a mineral acid. Other steps involved in recovery often vary, but mostly use solvent extraction and precipitation steps. In some processes, treatment with caustic soda yields indium hydroxide. The hydroxide is calcined to obtain oxide, which then is reduced with hydrogen at elevated temperatures to obtain the metal. Distillation or electrolysis are the final steps to

high purity metal.

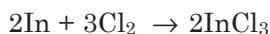
Reactions

Indium is stable in air at ambient temperature. At red heat, it oxidizes to indium trioxide, In_2O_3 . Three other oxides of indium are known: the suboxide, In_2O [12030-22], monoxide, InO [12136-26-4] and the sesquioxide, In_3O_4 [66525-54-0], which is a mixture of the trioxide and monoxide.

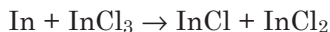
The most common valence state of indium is +3. However, +2 and +1 valence states also exist. Chemical properties of indium are similar to aluminum. Its redox potential is -0.34V . When heated with chlorine at 200°C , indium becomes a dichloride:



However, in the presence of excess chlorine, indium trichloride, InCl_3 is formed:



Similar reactions occur with other halogens. Monohalides of indium include chloride, bromide and iodide. Monohalides are obtained by passing indium trihalides over heated indium:

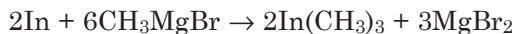


Indium dissolves in mineral acids. Concentration or evaporation of the solution produces corresponding salts. With sulfuric acid, it forms indium trisulfate, $\text{In}_2(\text{SO}_4)_3$ and indium hydrogen sulfate, $\text{In}(\text{HSO}_4)_2$. The latter salt is obtained upon concentration of trisulfate solution. With nitric acid, the salt is indium nitrate trihydrate, $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ [13770-61-1] which on dehydration yields monohydrate, $\text{In}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$.

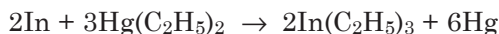
The metal combines with sulfur and phosphorous on heating, forming the sulfide and phosphide salts, respectively. Metalloid elements, such as arsenic, antimony, selenium and tellurium also combine with indium at elevated temperatures, forming their respective binary salts.

Indium combines with several metals, such as sodium, potassium, magnesium, iron, palladium, platinum, lanthanum and cerium, forming semiconductor-type intermetallic compounds.

Indium reacts with Grignard reagent, forming indium trialkyls which are highly flammable and less stable than the corresponding aluminum trialkyls:



The trialkyls also may be obtained by reaction of mercury dialkyls with indium:



Analysis

Indium produces characteristic lines in the indigo-blue region and may be detected by spectroscopic analysis. At trace concentrations In may be determined by flame-AA, furnace-AA, ICP-AES, x-ray fluorescence, or neutron activation analysis.

INDIUM ANTIMONIDE

[1312-41-0]

Formula: InSb; MW 236.58

Uses

Indium antimonide is used in semiconductor and Hall effect devices, and infrared detectors.

Physical Properties

Black cubic crystal; zincblende structure; density 5.775 g/cm³; melts at 525°C; density of melt 6.48 g/mL; dielectric constant 15.9; insoluble in water.

Thermochemical Properties

ΔH_f°	-7.30 kcal/mol
ΔG_f°	-6.10 kcal/mol
S°	20.6 cal/degree mol
C_p	11.82 cal/degree mol

Preparation

Indium antimonide may be synthesized from its elements by fusion of stoichiometric amounts of indium and antimony at elevated temperatures in an evacuated, sealed ampule.

Analysis

Elemental composition: In 48.53%; Sb 51.47%. The compound may be analysed by x-ray analysis. Also, both indium and antimony may be measured by AA or ICP spectrophotometry after digestion with aqua regia. The metals may be measured nondestructively by x-ray fluorescence technique.

INDIUM TRIOXIDE

[1312-43-2]

Formula: In₂O₃; MW 277.63

Synonym: indium(III) oxide

Uses

Indium trioxide is used to make special glasses and to impart yellow color to glass.

Physical Properties

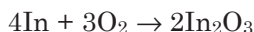
Light-yellow powder; cubic crystal; occurs in both amorphous and crystalline forms; pale-yellow amorphous form converts to crystalline form on heating at higher temperatures; isomorphous with hematite, Fe_2O_3 ; density 7.18 g/cm^3 ; melts around $2,000^\circ\text{C}$; insoluble in water; amorphous form dissolves readily in mineral acids; crystalline form has low solubility in acids.

Thermochemical Properties

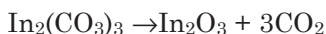
ΔH_f°	-221.27 kcal/mol
ΔG_f°	-198.54 kcal/mol
S°	$24.90 \text{ cal/degree mol}$
C_p	$21.99 \text{ cal/degree mol}$

Preparation

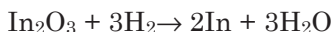
Indium trioxide may be obtained by heating indium in air or oxygen:



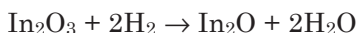
or by calcination of indium hydroxide, nitrate, or carbonate at elevated temperatures:

**Reactions**

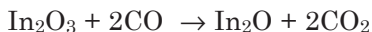
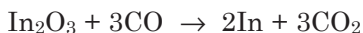
When heated with excess hydrogen at 450°C to 500°C , indium trioxide is reduced to indium metal:



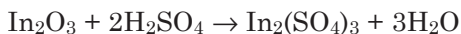
At lower temperatures or stoichiometrically lower amounts of hydrogen, lower oxides of indium are obtained:



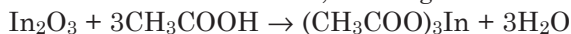
Similar reactions occur with carbon monoxide and other reducing gases:



Indium trioxide dissolves in sulfuric acid, forming indium trisulfate:



The oxide dissolves in acetic acid, forming indium triacetate:



Analysis

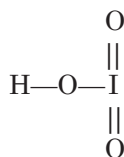
Elemental composition: In 82.71%, O 17.29%. Indium trioxide may be digested with nitric acid, diluted appropriately and analyzed for indium by AA or ICP. It may be identified by x-ray diffraction. The oxide may be heated with excess hydrogen and water formed may be analyzed quantitatively by gravimetry or the Karl-Fisher method.

IODIC ACID

[7782-68-5]

Formula: HIO_3 ; MW175.93; iodine in +5 oxidation state; solid acid contains $(\text{HO})\text{IO}_2$ molecules joined by hydrogen bonding; a monoprotic acid

Structure:



A pyro- form of the acid also is known. That has the formula HI_3O_8 .

Uses

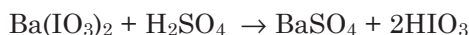
Aqueous solutions of iodic acid serve as strong oxidizing agents. The acid also is used in redox titrations.

Physical Properties

White stable crystalline solid; rhombohedral crystals; occurs in two forms: the normal HIO_3 , and pyroiodic acid HI_3O_8 .

Preparation

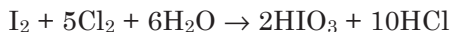
Iodic acid may be prepared by the reaction of sulfuric acid with barium iodate. The solution is filtered to remove barium sulfate and then crystallized to obtain iodic acid:



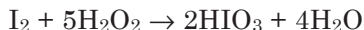
It also may be produced by oxidation of iodine with concentrated nitric acid:



Also, iodic acid may be obtained by oxidation of iodine with chlorine in dilute acidic solutions:



Another method of preparation involves oxidation of iodine with hydrogen peroxide:



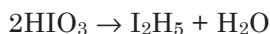
It also may be prepared by treating hypiodous acid with a base:



Hypiodous acid may be obtained by alkaline hydrolysis of iodine at pH 12:

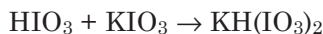


Iodic acid dehydrates to iodine pentaoxide when heated at 180°C:

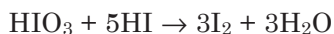
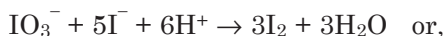


Iodic acid is a relatively weak monoprotic acid, the K_a value at 25°C is 1.6×10^{-1} . Several species have been detected in concentrated aqueous solutions, which include IO_3^- , H^+ , HIO_3 , $(\text{HIO}_3)_2$ and $(\text{HIO}_3)_3$. Its solution turns blue litmus red and then bleaches the litmus paper because of its strong oxidizing properties.

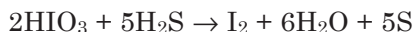
When heated with potassium iodate, potassium hydrogen iodate is formed:



An aqueous solution of iodic acid is a strong oxidizing agent. It liberates iodine from iodides:



In an aqueous solution, iodic acid oxidizes hydrogen sulfide to sulfur:



The solid iodic acid reacts vigorously with sulfur, phosphorus and other non-metals.

Analysis

Iodic acid can be analyzed by iodometric titration. Its acidic aqueous solution reacts with potassium iodide to liberate iodine (as shown above). Liberated iodine may be titrated against a standard solution of sodium thiosulfate using starch indicator. At the end point, the blue color of the solution

decolorizes.

IODINE

[7553-56-2]

Symbol I; atomic number 53; atomic weight 126.905; a nonmetallic halogen element of Group VII A (Group 17); occurs as a diatomic molecule; atomic radius 1.33Å; ionic (I^-) radius 2.20Å; the I—I bond length is 2.66Å and bond energy is 36.1 kcal/mol; electron configuration [Kr]4d¹⁰5s²5p⁵; electronegativity 2.2; common valence -1; also exhibits valence states +1, +3, +5 and +7; natural isotope I-127; several radioisotopes are known that range in mass numbers from 117 to 139.

History, Occurrence, and Uses

Iodine was discovered in 1811 by French chemist, Bernard Courtois during the production of potassium nitrate for Napoleon's armies. It was recognized as a new element by Gay-Lussac who named it iodine.

Iodine is widely distributed in nature, found in rocks, soils and underground brines. An important mineral is lautarite, which is anhydrous calcium iodate found in nitrate deposits in Chile. The element also occurs in brown seaweeds, in seawater, and in many natural gas wells. Its concentration in the earth's crust is an estimated 0.5 mg/kg; and in seawater 0.06 mg/L.

Iodine is used in many dyes and as a colorant for foods and cosmetics. Its silver salt is used in photographic negative emulsions. Other industrial applications include dehydrogenation of butane and butylenes to 1,3-butadiene; as a catalyst in many organic reactions; in treatment of naphtha to yield high octane motor fuel; and in preparation of many metals in high purity grade, such as titanium, zirconium and hafnium.

Iodine is an essential nutrient element required for thyroid gland. It is added to salt and to animal feeds for the prevention of goiter. In medicine it is used as a therapeutic reagent for the treatment of various thyroid-related diseases. It also is used as an antiseptic. Radioactive isotopes of iodine are used for treating thyroid cancer, heart diseases including tachycardia, and as a tracer for diagnosing certain diseases.

An important application of iodine is in water purification and sanitation. It is used as a disinfectant in food-processing plants, dairies and restaurants. It is applied to disinfect municipal and other water supplies and swimming pools.

Physical Properties

Bluish-black orthorhombic crystals; refractive index 3.34; density of solid 4.933 g/cm³ at 20°C; density of the element in liquid form at 120°C 3.96 g/cm³; melts at 113.6°C to a black mobile liquid; the solid can be sublimed to vapor below its melting point; vapor pressure of solid at 25°C 0.3075 torr; vapor pressure at 113.6°C 90.5 torr; the liquid boils at 184.3°C giving violet vapors; vapor density 6.75 g/L; critical temperature 545.8°C; critical pressure 48.9 atm; critical volume 155 cm³/mol; dielectric constant of solid 10.3 at 23°C and

liquid 11.08 at 118°C; resistivity 5.85×10^6 ohm-cm at 25°C, and 1.10×10^5 ohm-cm at 140°C; slightly soluble in water, 0.33 g/L at 25°C; soluble in ethanol, carbon disulfide, benzene and chloroform, forming brown solutions; sulfur, selenium, metal iodides and many organic compounds dissolve in liquid iodine.

Thermochemical Properties

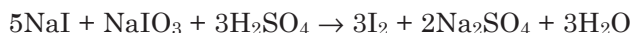
ΔH_f° (I ₂ crystal)	0.0
ΔH_f° (I ₂ gas)	14.91 kcal/mol
ΔH_f° (I gas)	25.53 kcal/mol
ΔG_f° (I ₂ gas)	4.61 kcal/mol
ΔG_f° (I gas)	16.78 kcal/mol
S° (I ₂ crystal)	27.75 cal/degree mol
S° (I ₂ gas)	62.31 cal/degree mol
S° (I gas)	43.21 cal/degree mol
C_p (I ₂ crystal)	13.00 cal/degree mol
C_p (I ₂ gas)	8.82 cal/degree mol
C_p (I gas)	4.97 cal/degree mol
ΔH_{fus} (I ₂ crystal)	3.71 kcal/mol
ΔH_{vap} (I ₂ liquid)	9.94 kcal/mol
ΔH_{sublim} (I ₂ crystal, at 113.6°C)	14.46 kcal/mol
Thermal conductivity (at 24.4°C)	0.421 W/(m.K)

Production

Iodine is produced in large scale from Chilean nitrate. Iodine occurs in this mineral as sodium iodate, NaIO₃. The iodate extract of the mineral becomes more concentrated in iodate after sodium nitrate crystallizes out. The mother liquor is then treated with sodium bisulfite solution to give sodium iodide:



The solution becomes acidic due to the formation of sulfuric acid. This solution is treated with an equivalent amount of fresh iodate mother liquor. Iodide-iodate reaction in acid medium yields iodine:



Iodine is separated by filtration or centrifugation, washed with water, dried and purified by sublimation.

In the United States and most parts of the world, iodine is obtained commercially from brine wells. Many subsurface brines have iodine concentrations in the range of 10 to 100 mg/L. Various extraction processes are known including: (i) precipitation with silver nitrate, (ii) oxidation with chlorine, and (iii) ion exchange. In the chlorine oxidation process, natural subsurface brine first is acidified with sulfuric acid and then treated with chlorine. Chlorine liberates iodine from the brine solution. Iodine is blown out into a counter-current stream of air. It is dissolved in a solution of hydriodic acid and sulfu-

ric acid by passing the iodine-enriched air through the solution. Treatment with sulfur dioxide reduces iodine to iodide. Iodine is finally recovered from the iodide solution in acid by oxidation with chlorine.

In the silver nitrate precipitation process, iodide in the brine is precipitated as silver iodide. The iodide is treated with iron to yield ferrous iodide. Passing chlorine through the ferrous iodide solution liberates iodine.

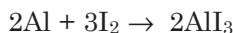
In the ion-exchange method, brine solution is passed through an anion-exchange resin. Iodide (and polyiodide) anions from the solution adsorb onto the resin from which they are desorbed by treatment with caustic soda solution. The resin is treated with sodium chloride solution to regenerate its activity for reuse. The iodide solution (also rich in iodate, IO_3^- ions) is acidified with sulfuric acid. The acid solution is oxidized to precipitate out iodine. Iodine is purified by sublimation.

Iodine is packed and supplied in polyethylene-lined fiber drums or high silicon iron, Hastelloy B, or lead coated steel containers. Glass, graphite and acid-proof bricks are very suitable for storing iodine and its solutions.

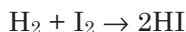
Reactions

Chemical properties of iodine are quite similar to those of other halogens, especially chlorine and bromine. However, being less electronegative than chlorine and bromine, its reactivity towards most metals, nonmetals, and their compounds may differ vastly. All iodine reactions occur in vapor phase or aqueous media. Vapor phase reactions require elevated temperatures.

Iodine vapors combine with metals forming their iodides. The rates of such reactions vary with metals, their states, and temperatures. The reaction is very rapid when the metal is in finely divided state, and slow when the metal is in massive form.



Heating with hydrogen at high temperatures gives hydrogen iodide:

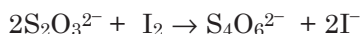


In aqueous solutions, iodine hydrolyzes to hypiodous acid, hydrogen ion and iodide anion:

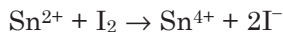


The equilibrium constant for the above reaction is 5.0×10^{-15} at 25°C .

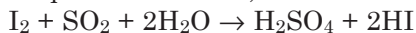
In acid solution, iodine is a weak oxidizing agent. The redox potential is -0.534 V at 25°C . It readily oxidizes thiosulfate to tetrathionate ion:



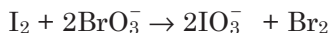
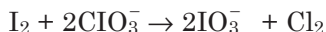
Similarly, it oxidizes SO_3^{2-} , Sn^{2+} , and Ti^{2+} ions in acid solution to SO_4^{2-} , Sn^{4+} , and Ti^{4+} , respectively:



In dilute aqueous solutions, iodine oxidizes sulfur dioxide to sulfuric acid:



In acid solutions, iodine reduces powerful oxidizing agents and is oxidized itself. For example, it reduces chlorate and bromate to chlorine and bromine, respectively, and nitric acid to nitric oxide. In all these reactions, iodine is oxidized to iodate:



Iodine behaves as a powerful oxidizing agent in strong alkaline solution due to the formation of hypoiodite ion:



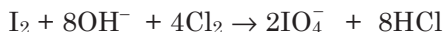
The hypoiodite ion, however, is unstable, decomposing to iodate and iodide ions:



Thus, when the overall reaction in aqueous base goes to completion at higher temperatures, the reaction may be written as:



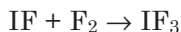
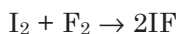
When chlorine is passed through an alkaline solution of iodine, the latter is oxidized to periodate:



Reaction with iodic acid and hydrochloric acid produces iodine monochloride:



Iodine combines with fluorine, chlorine and bromine, forming interhalogen compounds such as ICl , IBr_5 , IF_7 . Fluorine successively adds on to iodine forming mono-, tri-, penta-, and heptafluorides of iodine:

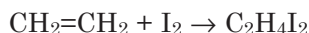




The oxidation state of iodine in iodine heptafluoride is +7.

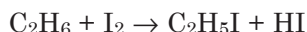
Iodine partially dimerizes in organic solvents, forming tetraatomic I_4 species.

Among organic compounds, alkenes readily react with iodine, giving addition products. For example, iodine adds to ethylene, forming ethylene diiodide:



Such reactions are reversible and the presence of free iodine decomposes the products back to alkenes.

Substitution reactions occur at high temperatures:



The yield is higher in basic solution in the presence of an oxidizing agent. Iodine forms a blue complex with β -amylose in starch. A linear array of I_5^- species consisting of $\text{I}_2 - \text{I}^- - \text{I}_2$ units bound to the amylose helix causes blue color formation.

Analysis

Free iodine may be determined from its color and physical properties.

Iodine in aqueous solution may be measured quantitatively by acidifying the solution, diluting it, and titrating against a standard solution of sodium thiosulfate, sodium arsenite or phenyl arsine oxide using starch indicator. The blue color of the starch decolorizes at the end point. The indicator must be added towards the end of titration when the color of the solution turns pale yellow. Prior to titration, iodine in the dilute acidic solution is oxidized to iodate by adding bromine water or potassium permanganate solution. Excess potassium iodide is then added. The liberated iodine is then titrated as above.

Iodine in water also may be determined by the Leucocrystal violet colorimetric method. An aqueous sample is treated with mercuric chloride followed by Leucocrystal violet reagent [4,4',4''-methylidynetris(N,N-dimethylaniline)] in the pH range 3.5 to 4.0. A violet color is produced. The absorbance or transmittance is measured at 592 nm by a spectrophotometer or filter photometer. Iodine concentration is calculated from a standard calibration curve.

All forms of iodine including the elemental iodine, hypoiodous acid (HOI), hypoiodite anion (OI^-), free iodide anion (I^-), and triiodide anion (I_3^-) in water also may be measured by the Leuco crystal violet method. The sample is treated with potassium peroxymonosulfate to oxidize all iodide species in the sample. It then is treated with leukocrystal violet reagent for color development. Interference from free chlorine may be eliminated by addition of an ammonium salt.

Iodide ion may be measured by amperometric titration and, more accurately, by ion chromatography.

Toxicity

Iodine vapors are an irritant to eyes, nose and mucous membranes. Inhalation can cause headache, irritation, and congestion of lungs. Oral intake can produce burning of the mouth, vomiting, diarrhea, and abdominal cramps. Skin contact can cause rashes.

IODINE HEPTAFLUORIDE

[16921-96-3]

Formula: IF₇; MW 221.90; pentagonal bipyramidal structure.

Synonym: heptafluoroiodine

Uses

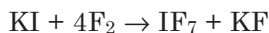
Iodine heptafluoride is used as a fluorinating agent.

Physical Properties

Colorless gas; mold-like pungent odor; melting point 6.45°C; sublimes at 4.77°C; supercools to a colorless liquid that boils at 4.5°C; liquid density 2.8g/mL at 6°C; soluble in water.

Preparation

Iodine heptafluoride may be prepared by the reaction of fluorine with potassium iodide:



Dried KI should be used to minimize the formation of IOF₅.

Also, IF₇ can be prepared by passing fluorine gas through liquid iodine pentafluoride at high temperature (90°C) and then heating the vapors to 270°C to complete the reaction:



Reactions

Most reactions of iodine heptafluoride are similar to those of iodine pentafluoride, except that it does not undergo any further fluorine addition reactions (See Iodine Pentafluoride). The compound reacts with a number of inorganic substances, forming their fluorides, and forms fluoro-derivatives with organics when in diluted form.

Toxicity

The compound is corrosive. Vapors are highly irritating to eyes and mucous

membranes.

IODINE MONOCHLORIDE

[7790-99-0]

Formula: ICl; MW 162.357

Synonyms: Wijs' chloride; iodine chloride

Uses

Iodine monochloride is used as an analytical reagent to determine iodine values of oils and fats. It is dissolved in glacial acetic acid (Wijs' solution) for the analysis. ICl is used in organic synthesis. It also is used as a topical anti-septic.

Physical Properties

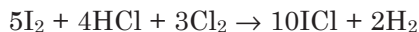
Black crystalline solid; exists in two modifications: stable black needles known as alpha form that produces ruby-red color in transmitted light, and a labile, metastable beta modification consisting of black platelets which appear brownish-red in transmitted light; density of alpha form 3.86 g/cm³ at 0°C; density of beta form 3.66 g/cm³ at 0°C; alpha form melts at 27.3°C, vapor pressure being 28 torr at 25°C; beta form melts at 13.9°C; liquid iodine monochloride has bromine-like reddish-brown color; liquid density 3.10 g/mL at 29°C; viscosity 1.21 centipoise at 35°C; decomposes around 100°C; supercools below its melting point; polar solvent; as a liquid it dissolves iodine, ammonium chloride and alkali metal chlorides; liquid ICl also miscible with carbon tetrachloride, acetic acid and bromine; the solid crystals dissolve in ethanol, ether, acetic acid and carbon disulfide; solid ICl also dissolves in conc. HCl but decomposes in water or dilute HCl.

Thermochemical Properties

ΔH_f° (liq)	-5.712 kcal/mol
ΔH_f° (gas)	4.254 kcal/mol
ΔG_f° (liq)	-3.250 kcal/mol
ΔG_f° (gas)	-1.315 kcal/mol
S° (liq)	32.29 cal/degree mol
S° (gas)	59.18 cal/degree mol
C_p (liq)	0.0257 cal/degree mol
C_p (gas)	8.51 cal/degree mol
ΔH_{fus}	2.77 kcal/mol
ΔH_{vap}	9.95 kcal/mol

Preparation

Iodine monochloride is prepared by the action of liquid or dry chlorine on a stoichiometric quantity of solid iodine. Aqueous solutions of ICl are prepared by passing chlorine gas into a suspension of iodine in moderately strong hydrochloric acid:

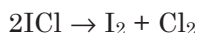


Alternatively, iodine monochloride may be made by oxidation of iodine with iodic acid in strong hydrochloric acid solution:

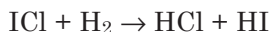


Reactions

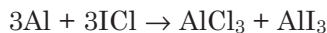
When vaporized at 100°C iodine monochloride decomposes to chlorine and iodine:



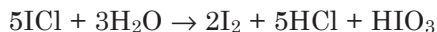
Heating with hydrogen at elevated temperatures yields hydrogen chloride and hydrogen iodide:



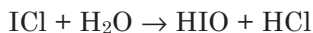
Reactions with metals in a finely-divided state or at elevated temperatures, produce metal chlorides and metal iodides:



It hydrolyzes in water, decomposing to iodine, hydrochloric acid and iodic acid:

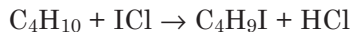


Under milder conditions and in equimolar ratio, hypiodous acid forms:

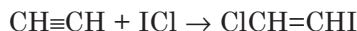


Similar hydrolysis occurs in dilute HCl.

Reactions with alkanes produce iodo derivatives and hydrogen chloride:



Iodine monochloride adds to unsaturated compounds. Some examples are:



Analysis

Elemental composition: Cl 21.84%, I 78.16%. The compound is hydrolyzed in water and the product chloride and iodate ions are analyzed by ion chro-

matography. Iodine is separated by filtration and measured by gravimetry or by the Leuco Crystal violet colorimetric method (See Iodine). Alternatively, the liquid or solid compound is dissolved in organic solvent, diluted appropriately, and analyzed by GC/MS.

IODINE PENTAFLUORIDE

[7783-66-6]

Formula: IF₅; MW 221.90; square pyramidal structure.

Uses

Iodine pentafluoride is a fluorinating agent. It also is used in incendiaries.

Physical Properties

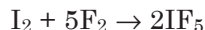
Colorless to yellowish liquid; fumes in air; density 3.19 g/mL; freezes at 9.43°C; boils at 100.5°C; reacts with water.

Thermochemical Properties

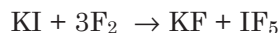
ΔH_f° (l)	-206.7 kcal/mol
ΔH_f° (g)	-196.6 kcal/mol
ΔG_f° (g)	-179.7 kcal/mol
S° (g)	78.3 cal/degree mol
C_p	23.7 cal/degree mol
ΔH_{vap}	9.87 kcal/mol

Preparation

Iodine pentafluoride is best obtained by passing fluorine gas over iodine under cooling conditions:



Also, it may be prepared by the reaction of fluorine with iodine trifluoride; or heating potassium iodide with a stoichiometric amount of fluorine:



Reactions

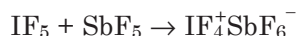
Thermal dissociation of iodine pentafluoride yields iodine trifluoride and fluorine:



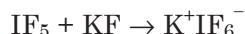
It combines with fluorine, forming iodine heptafluoride:



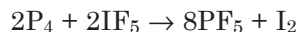
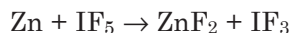
Iodine pentafluoride similar to other halogen fluorides exhibits amphoteric behavior; i.e., with strong Lewis acids, such as SbF_5 , it can form cation, IF_4^+ :



Similarly, with strong bases like potassium fluoride, it forms the anion IF_6^- :



Iodine pentafluoride reacts with many inorganic substances, forming their fluorides. Such inorganic substances include metals, metal oxides and several nonmetals. Some examples are:



It reacts violently with water, forming hydrogen fluoride and iodic acid:



Iodine pentafluoride reacts with organic substances, forming their fluoro-derivatives only when it is diluted with nitrogen. The pure compound may otherwise carbonize organics on contact, sometimes violently.

Analysis

Elemental composition: I 57.19%, F 42.81%. The compound may be hydrolyzed with water slowly and cautiously (a violent reaction occurs). Iodate anion may be measured by redox titration and the fluoride ion by using a fluoride ion-selective electrode. Alternatively, these anions in their aqueous solution may be determined by ion chromatography after appropriate dilution.

Hazard

Most reactions are violent. Accidental contact with a number of organics and inorganic substances may present a fire or explosion hazard. Rapid mixing with water can be explosive. The compound is highly corrosive. Skin contact can cause a severe burn. Vapors are highly irritating to eyes, nose and mucous membranes. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd. Ed. New York: John Wiley & Sons.)

IODINE PENTOXIDE

[12029-98-0]

Formula: I_2O_5 ; MW 333.81

Uses

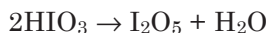
Iodine pentoxide is used for analysis of carbon monoxide and for CO removal from air. It also is used as an oxidizing agent in other oxidation reactions.

Physical Properties

White crystals; hygroscopic; density 4.98 g/cm^3 ; decomposes around 300°C ; highly soluble in water; soluble in nitric acid; insoluble in ethanol, ether and carbon disulfide.

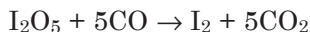
Preparation

Iodine pentoxide is prepared by dehydration of iodic acid at 240°C .



Reactions

Iodine pentoxide is a strong oxidizing agent and reacts with various oxidizable substances. It oxidizes carbon monoxide to carbon dioxide. The reaction is quantitative and used to measure carbon monoxide in the air:



It reacts with hydrogen sulfide, forming sulfur dioxide:



Oxidation reaction also occurs with hydrogen chloride, metal hydrides and a number of metal salts. It dissolves in water reacting to form iodic acid:



Dissociation into iodine and oxygen commences when heated above 270°C .

IODINE TRICHLORIDE

[865-44-1]

Formula: ICl_3 ; MW 233.262

Uses

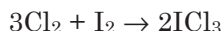
Iodine trichloride is used in organic synthesis as a chlorinating and iodinating agent to introduce chlorine and iodine into organic compounds producing their halogen derivatives. It also is used as a topical antiseptic.

Physical Properties

Orange yellow triclinic crystals or fluffy powder; hygroscopic; density 3.111 g/cm³ at 15°C; sublimes at 64°C with decomposition; melts at 101°C at 16 atm; hydrolyzes in water; soluble in ethanol, carbon tetrachloride and benzene; soluble in concentrated hydrochloric acid but hydrolyzes in dilute acid.

Preparation

Iodine trichloride is prepared by adding iodine to liquid chlorine in a stoichiometric amount:

**Reactions**

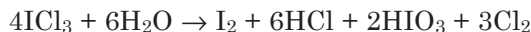
Iodine trichloride decomposes on heating at 77°C, forming iodine monochloride and chlorine:



It dissolves in concentrated hydrochloric acid, forming $\text{HICl}_4 \cdot 4\text{H}_2\text{O}$:



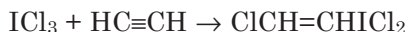
Iodine trichloride hydrolyzes in water or dilute acids, the products depending upon reaction conditions. This reaction usually is similar to iodine monochloride:



It combines with potassium chloride, forming a complex salt, KICl_4 :



Reaction with acetylene produces chlorovinyl iododichloride, containing two active chlorine atoms attached to the iodine atom:



The above product has many applications in chemical synthesis..

Toxicity

Iodine trichloride is highly corrosive. Contact with skin can cause a burn. Vapors are highly irritating to eyes and respiratory tract.

IRIDIUM

[7439-88-5]

Symbol: Ir; atomic number 77; atomic weight 192.22; a Group VIII (Group 8) transition metal; electron configuration $[\text{Xe}]4f^{14}5d^76s^2$; common valence states +3 and +4; valence states 0, +1, +2, +5 and +6 are known; two natural isotopes, Ir-191 (37.30%) and Ir-193 (62.70%) The element has 28 radioisotopes, ranging in masses from 170 to 198.

History, Occurrence, and Uses

Iridium metal was detected in the black residue of aqua regia extract of platinum and identified as an element by British chemist Smithson Tennant in 1803. Around the same time, existence of this new metal was proposed by Vauquelin and deFourcroy in France in the course of their extraction of platinum by aqua regia. Tennant named this element Iridium after the Greek word, Iris, meaning rainbow.

Iridium occurs in small amounts in native platinum or platinum metal alloys. Iridium and osmium together constitute "osmiridium," which is resistant to chemical attack and is a byproduct of platinum extraction.

The most important use of iridium is as an alloying metal for platinum and palladium. Such alloys are used for jewelry, decorative purposes, electrical contacts, thermocouples, crucibles, electrodes, hypodermic needles, and medical accessories. Iridium enhances resistance of platinum to chemical attack and corrosion. It also enhances hardness and tensile strength. The radioisotope Ir-192 is used in examination of ferrous welds and in other radiographic applications.

Physical Properties

Silvery-white metal; close-packed cubic crystals; lattice constant 3.8394 Å at 20°C; density 22.42 g/cm³ (highest among metals); melts at 2410°C; vaporizes at 4,130°C; hardness 6–6.5 Mohs; electrical resistivity 4.71 μohm-cm; Young's modulus 3.75 x 10⁴ tons/in²; magnetic susceptibility 0.133 x 10⁻⁶ cm³/g; thermal neutron absorption cross section 440 barns.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	159.0 kcal/mol
ΔG_f° (gas)	147.87 kcal/mol
S° (cry)	8.48 cal/degree mol
S° (gas)	46.24 cal/degree mol
C_p (cry)	6.00 cal/degree mol
C_r (gas)	4.97 cal/degree mol
Thermal conductivity (0-100°C)	1.48 watts/cm/°C
Coeff. linear expansion (20 to 100°C)	6.8 x 10 ⁻⁶ /°C

Reactions

At ordinary temperatures iridium exhibits strong resistance to chemical

attack. At elevated temperatures of about 600°C, iridium metal combines with oxygen to form a coating of iridium dioxide, IrO_2 . Similarly, the metal reacts with halogens only at elevated temperatures. It reacts with fluorine at 250°C, forming iridium hexafluoride, IrF_6 , and, to a lesser extent, iridium tetrachloride IrCl_4 . Heating with chlorine at 600°C produces iridium trichloride, IrCl_3 . Iridium forms alloys with several metals—mostly platinum group metals.

Iridium does not react with concentrated acids or with molten alkalis.

Analysis

Iridium may be analyzed by x-ray. Also, AA or ICP measurements may be performed after digestion in hot acid mixture. The metal is practically insoluble in all mineral acids and aquaregia, even on heating. A 20:1 mixture of $\text{HCl}:\text{HNO}_3$ may be used to dissolve it with strong heating.

IRON

[7439-89-6]

Symbol: Fe; atomic number 26; atomic weight 55.847; a Group VIII (Group 8) metallic element; transition metal; atomic radius 1.24Å; electron configuration $[\text{Ar}]3d^64s^2$; most common valence states +2 and +3; other oxidation states -1, 0, +1, +4 and +6 are known but rare; most abundant isotope Fe-56; natural isotopes and their abundances: Fe-54 (5.90%), Fe-56 (91.52%), Fe-57 (2.245%), Fe-58 (0.33%).

History, Occurrence, and Uses

Iron has been known to mankind from early civilization. In fact, a period of history, the “iron age,” is named for the widespread use of this metal. For almost a thousand years, it remained as the single most-used metal, and its use in mechanization made the industrial revolution possible.

Iron, after oxygen, silicon and aluminum, is the fourth most abundant element in the earth's crust. It is the prime constituent of earth's core along with nickel. Its abundance in the crust is 5.63%. Its concentration in the seawater is about 0.002mg/L. The principal ores of iron are hematite, Fe_2O_3 ; pyrite, Fe_2S_2 ; ilmenite, FeTiO_3 ; magnetite, Fe_3O_4 ; siderite, Fe_2CO_3 ; and limonite $[\text{FeO}(\text{OH})]$. It also is found in a number of minerals, such as corundum, as an impurity. It also is found in meteorites.

Iron occurs in every mammalian cell and is vital for life processes. It is bound to various proteins and found in blood and tissues. The iron-porphyrin or heme proteins include hemoglobin, myoglobin and various heme enzymes, such as cytochromes and peroxidases. Also, it occurs in non heme compounds, such as ferritin, siderophilin, and hemosiderin. Hemoglobin, found in the red blood cells, is responsible for transport of oxygen to the tissue cells and constitutes about two-thirds (mass) of all iron present in the human body. An adult human may contain about 4 to 6 grams of iron.

Industrial uses of iron as carbon steels are numerous and surpass any

other alloys. Carbon steels are alloys of iron containing carbon in varying proportions, usually up to 1.7% carbon. Other metals also are incorporated into carbon steels to produce low-alloy steels. Such metals are usually nickel and chromium and are classified as stainless steel, tool steels, and heat-resistant steels. Non-steel iron alloys such as cast iron, wrought iron, nickel iron and silicon iron also have many important applications.

Another important application of iron is as an industrial catalyst. It is used in catalyst compositions in the Haber process for synthesis of ammonia, and in Fischer-Tropsch process for producing synthetic gasoline.

Physical Properties

Soft white, ductile metal; high-purity metal is very ductile at ordinary temperatures; occurs in three allotropic forms: (i) body-centered cubic form, alpha iron stable up to 910°C, (ii) face-centered cubic form, gamma iron occurring between 910 to 1,390°C, and (iii) body-centered delta iron allotope forming above 1,390°C. Density 7.873 g/cm³ at 20°C; melting point 1,538°C; vaporizes at 2,861°C; hardness (Brinell) 60; electrical resistivity 4.71 microhm-cm at 0°C; tensile strength 30,000 psi; Poisson's ratio 0.29; modulus of elasticity 28.5 x 10⁶ psi; thermal neutron absorption cross-section 2.62 barns; velocity of sound 5,130 m/s at 20°C.

Molten iron: Density 7.00 g/cm³ at 1,564°C; vapor pressure 0.06 torr at 1,600°C, and 1 torr at 1,850°C, respectively; viscosity 4.45 centipoise at 1,743°C; surface tension 1,835-1,965 dynes/cm; electrical resistivity 139 microhm-cm at the melting point. Magnetic properties: attracted by magnets; rapidly loses its magnetism; ferromagnetic at ordinary temperature; becomes paramagnetic when heated to its Curie point, 768°C.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	99.5 kcal/mol
ΔG_f° (gas)	88.6 kcal/mol
S° (cry)	6.52 cal/degree mol
S° (gas)	43.1 cal/degree mol
C_p (cry)	6.00 cal/degree mol
C_p (gas)	6.14 cal/degree mol
ΔH_{fus}	3.30 kcal/mol
Latent heat of fusion	65.5 cal/g
Latent heat of vaporization	1,598 cal/g
Coeff. linear expansion:	
Alpha form (20-100°C)	23.04 x 10 ⁻⁶ /°C
Gamma form (916-1388°C)	23.6 x 10 ⁻⁶ /°C
Delta form (1388-1502°C)	9.7 x 10 ⁻⁶ /°C
Thermal conductivity (at 0°C)	0.2 cal/cm/sec/°C

Production

Most iron produced today is from its oxide minerals, hematite and magnetite. The process involves reducing mineral iron with carbon in a blast fur-

nace. There are several types of blast furnaces which vary in design and dimensions. The overall processes, however, are more or less the same. One such process is outlined below:

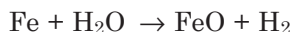
The mixture of ore, coke and limestone is fed into the blast furnace from the top. The materials are preheated to about 200°C in the top most zone. Hematite is partially reduced to magnetite and then to FeO by the ascending stream of carbon monoxide formed at the bottom and mid zones of the furnace resulting from high temperature oxidation of carbon. The ferrous oxide FeO formed at the top zone is reduced to metallic iron at about 700°C in the mid zone by carbon monoxide. A hot air blast at 900°C passes through the entire furnace for a very short time (usually for a few seconds). This prevents any gas-solid reaction product from reaching equilibrium. In the temperature zone 700 to 1,200°C ferrous oxide is completely reduced to iron metal by carbon monoxide. Also, more CO is formed by oxidation of carbon by carbon dioxide. Further down the furnace at higher temperatures, around 1,500°C, iron melts, dripping down into the bottom. Also, in this temperature zone acidic silica particles react with basic calcium oxide produced from the decomposition of limestone, producing calcium silicate. The molten waste calcium silicate also drips down into the bottom. In the hottest zone of the blast furnace, between 1,500 to 2,000°C, some carbon dissolves into the molten iron. Also at these temperatures any remaining silicates and phosphates are reduced to silicon and phosphorus, and dissolve into the molten iron. Additionally, other tract metals such as manganese dissolve into the molten iron. The impure iron melt containing about 3 to 4% carbon is called “pig iron”. At the bottom, the molten waste slag floats over the impure pig iron melt that is heavier than the slag melt and immiscible with it. Pig iron is separated from the slag and purified for making different types of steel. Chemical reactions and processes occurring in various temperature zones of blast furnace are summarized below:

<i>Top preheating zone:</i>	
200°C	$3\text{Fe}_2\text{O}_3(\text{s}) + \text{CO}(\text{g}) \xrightarrow{\text{reduction}} 2\text{Fe}_3\text{O}_4(\text{s}) + \text{CO}_2(\text{g})$ $\text{Fe}_2\text{O}_4(\text{s}) + \text{CO}(\text{g}) \xrightarrow{\text{reduction}} 2\text{FeO}(\text{s}) + \text{CO}_2(\text{g})$ $\text{CaCO}_3(\text{s}) + \text{CO}(\text{g}) \xrightarrow{\text{decomposition}} \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
<i>Mid zone:</i>	
700°	$\text{FeO}(\text{s}) + \text{CO}(\text{g}) \xrightarrow{\text{reduction}} \text{Fe}(\text{s}) + \text{CO}_2(\text{g})$ $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \xrightarrow[\text{carbon}]{\text{oxidation}} 2\text{CO}(\text{g})$
1,200-1,500°C	$\text{Fe}(\text{s}) \xrightarrow{\text{melting}} \text{Fe}(\text{l})$ $\text{CaO}(\text{s}) + \text{SiO}_2(\text{s}) \xrightarrow[\text{slag}]{\text{formation}} \text{CaSiO}_3(\text{l})$
<i>Bottom zone:</i>	
1,500-2,000°C	$\text{phosphates} \xrightarrow{\text{reduction}} \text{P} + \text{O}_2$ $\text{silicates} \xrightarrow{\text{reduction}} \text{Si} + \text{O}_2$ $\text{C, P, Si, Mn, ...}(\text{s}) + \text{Fe}(\text{l}) \xrightarrow{\text{dissolution}} \text{pig iron}(\text{l})$
2,000°C	$2\text{C}(\text{s}) + \text{O}_2(\text{g}) \xrightarrow{\text{oxidation}} 2\text{CO}(\text{g}) + \text{heat}$

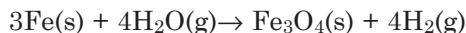
Pig iron produced in the blast furnace is purified and converted to steel in a separate furnace, known as a basic-oxygen furnace. Jets of pure oxygen gas at high pressure are blown over and through the pig iron melt. Metal impurities are converted into oxides. Part of the dissolved carbon in the impure iron melt is converted into carbon dioxide gas. Formation of SiO_2 , CO_2 , and other metal oxides are exothermic reactions that raise the temperature to sustain the melt. A lime flux (CaO) also is added into the melt, which converts silica into calcium silicate, CaSiO_3 , and phosphorus into calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, forming a molten slag immiscible with molten steel. The lighter molten slag is decanted from the heavier molten steel.

Reactions

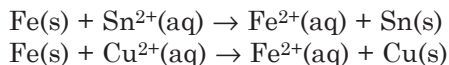
The most common oxidation states of iron are +2 (ferrous) and +3 (ferric). The standard electrode potential for $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$ is -0.440 volts. Thus, the metal can replace hydrogen from water at ordinary temperatures:



The reaction, however, is slow at room temperature, but rapid above 500°C . Decomposition of steam when passed over hot iron filings was discovered by Lavoisier:



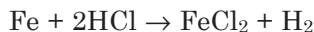
Iron also exhibits single replacement reactions, precipitating less electropositive metals out of their salt solutions. Thus, solid iron can reduce many metals, such as copper, silver, gold, mercury, tin and nickel:



Solid iron undergoes rusting by reacting with oxygen in the presence of water (or water vapor). Thus, in moist air, it rapidly converts to rust, which is hydrous iron(III) oxide. The reaction occurs at ordinary temperatures, catalyzed by acid. The overall reaction is:



Iron dissolves in mineral acids. In nonoxidizing acids, such as HCl or H_2SO_4 , and in the absence of air or oxidizing agents, the metal is oxidized to ferrous state (Fe^{2+}) liberating hydrogen:



In air, Fe^{2+} is partially oxidized to (ferric) ion. With warm dilute nitric acid, the product mixture contains both Fe^{2+} and Fe^{3+} ions.

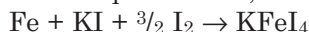
Hot dilute nitric acid reacts with iron, forming ferric nitrate, $\text{Fe}(\text{NO}_3)_3$. Also, nitrogen oxides evolve in the reaction, probably from decomposition of

nitric acid catalyzed by iron.

No reaction occurs with concentrated nitric acid nor with a strong oxidizing agent such as $\text{Cr}_2\text{O}_7^{2-}$ ion. Iron also does not precipitate out other metals in such concentrated nitric acid or other strong oxidizing medium. Such “passivating effect” of concentrated nitric acid on iron is attributed to formation of an oxide film on the metal surface. The passivating oxide film can be removed by treatment with reducing agents or by scratching the metal surface.

Iron reacts with nonmetals forming their binary compounds. It combines readily with halogens. Reaction is vigorous with chlorine at moderate temperature. With oxygen, it readily forms iron oxides at moderate temperatures. In a finely divided state, the metal is pyrophoric. Iron combines partially with nitrogen only at elevated temperatures. It reacts with carbon, sulfur, phosphorus, arsenic, and silicon at elevated temperatures in the absence of air, forming their binary compounds.

When heated with iodide of potassium, rubidium, or cesium and iodine at 300°C in a sealed quartz tube, iron forms tetraiodide complex anion, FeI_4^- :



Analysis

Iron metal can be analyzed by x-ray spectroscopy, flame- and furnace atomic absorption, and ICP atomic emission spectroscopy at trace concentration levels. Other instrumental techniques include ICP-mass spectrometry for extreme low detection level and neutron activation analysis.

Several colorimetric methods also are known in which various organic complexing agents are used. One such method involves complexing iron with 1,10-phenanthroline. The metal is dissolved and reduced to Fe^{2+} state by boiling in an acid with excess hydroxylamine. The solution then is treated with 1,10-phenanthroline. An orange-red color develops rapidly in the pH range of 3.2 to 3.3. The concentration of iron in the solution is proportional to the absorbance or transmittance measured at 510nm. This analytical method may be applied to distinguish ferrous iron from the ferric form. X-ray methods may be applied on solid samples without dissolving the metal samples.

IRON(II) AMMONIUM SULFATE

[10045-89-3]

Formula: $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$; MW 392.14; occurs as hexahydrate

Synonyms: ferrous ammonium sulfate; ammonium ferrous sulfate; Mohr's salt.

Uses

Iron ammonium sulfate is an analytical reagent in titrations and colorimetric measurements to measure oxidizing substances, such as chlorine, or to measure the chemical oxygen demand in waste water. The compound is used to prepare Fe(II) standard solution for these analyses. It also is a calibration

standard in magnetic measurements; a reducing agent; a catalyst for polymerization; and is used in photographic chemistry.

Physical Properties

Bluish-green monoclinic crystal; density 1.86 g/cm³; decomposes at 100°C; soluble in water; insoluble in alcohol.

Preparation

Ferrous ammonium sulfate may be prepared by mixing an equimolar solution of ferrous sulfate and ammonium sulfate, followed by evaporation and crystallization.

Analysis

Elemental composition: Fe 19.66%, H 2.84%, N 9.86%, O 45.06%, S 22.57%. It may be analyzed by titrating against a standard solution of an oxidizing agent. Also, iron content of the compound can be determined by AA, ICP or x-ray analysis.

IRON(III) AMMONIUM SULFATE

[10138-04-2]

Formula: $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; MW 482.19

The compound occurs as dodecahydrate containing 12 molecules of water of crystallization.

Synonyms: ferric ammonium sulfate; ammonium ferric sulfate; iron alum; ferric alum; ferric ammonium alum

Uses

Iron(III) ammonium sulfate is a mordant in dyeing and printing of fabrics and textiles. The compound also is an analytical reagent; and is used in medicine.

Physical Properties

The dodecahydrate is lilac to violet crystal (anhydrous compound is colorless); density 1.71 g/cm³; melts around 37°C; hydrated crystals lose all water molecules at 230°C; readily dissolves in water; insoluble in alcohol; aqueous solution is acidic.

Preparation

Ferric ammonium sulfate is prepared by mixing an equimolar solution of ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3$, and ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$. Hydrated crystals are obtained following evaporation and cooling of the solution.

Analysis

Elemental composition: Fe 21.00%, H 1.52%, N 5.27%, O 48.12%, S 24.10%. Iron content in the compound may be measured by various instrumental techniques (See Iron).

IRON(III) BROMIDE

[10031-26-2]

Formula: FeBr₃; MW 295.56

Synonym: ferric bromide; iron tribromide

Uses

Iron(III) bromide is a catalyst in bromination of aromatic compounds.

Physical Properties

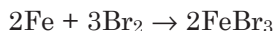
Dark red hexagonal crystal; hygroscopic; partially decomposes to FeBr₂, losing some bromine on exposure to air or light; density 4.50 g/cm³; decomposes on heating; soluble in water, ethanol, and ether.

Thermochemical Properties

ΔH_f° -61.10 kcal/mol

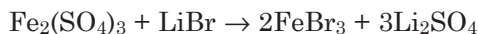
Preparation

Iron(III) bromide is prepared by the action of bromine with iron filings:



The compound should be stored in dark bottles protected from air or light.

It also may be obtained by double decomposition reactions between a ferric salt and a bromide (alkali metal bromide) in aqueous solution followed by evaporation and crystallization:



It also may be prepared in high yield by photochemical reaction of dibromotetracarbonyl with bromine in hexane (Yoon, K.B. and J.K. Kochi. 1990. *Inorg. Chem.* 29, pp. 869):

**Reactions**

The aqueous solution of iron(III) bromide decomposes to iron(II) bromide and bromine on boiling:



It is reduced by iron in tetrahydrofuran forming iron(II) bromide:



Iron(III) bromide forms several adduct with donor molecules in solutions. For

example, with triphenylphosphine, $(\text{P}(\text{C}_6\text{H}_5)_3)$, it forms trigonal bipyramidal complex, $\text{FeBr}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$.

Analysis

Elemental composition: Fe 18.89%, Br 81.11%. The solid material may be analyzed nondestructively by x-ray techniques. The aqueous solution may be acidified with nitric acid (to prevent reduction) and analyzed for iron without further hot digestion by AA or ICP techniques. The bromide ion may be best determined by ion chromatography following appropriate dilution.

IRON CARBONYLS

Iron forms a few carbonyl compounds in all of which the valence state of iron is zero. The names, CAS numbers, formulas and molecular weights of known iron carbonyls are:

Iron pentacarbonyl	[13463-40-6]	$\text{Fe}(\text{CO})_5$	195.90
Iron nonacarbonyl	[15321-51-4]	$\text{Fe}_2(\text{CO})_9$	363.78
Iron dodecacarbonyl	[12088-65-2]	$\text{Fe}_3(\text{CO})_{12}$	503.66
Iron hydrocarbonyl	[17440-90-3]	$\text{H}_2\text{Fe}(\text{CO})_4$	169.90

Uses

Iron pentacarbonyl is the most important carbonyl compound of iron. It is used primarily to produce finely divided iron metal. Other applications are in catalysis of organic reactions; in ceramics; as an anti-knock in gasoline; and in production of red iron oxide pigment. Other carbonyls of iron have very few commercial applications.

Physical Properties

Iron pentacarbonyl is a yellow oily liquid; flammable; density 1.490 g/mL; freezes at -20°C ; boils at 103°C ; vapor pressure 40 torr at 30°C ; insoluble in water; slightly soluble in ethanol; soluble in acetone, ether, and benzene.

The nonacarbonyl is an orange-yellow crystalline solid at ambient temperatures; density 2.85 g/cm³; decomposes at 100°C . Iron dodecacarbonyl is a black crystalline solid; density 2.0g/cm³; decomposes at 140°C . Iron hydrocarbonyl is an unstable colorless liquid; solidifies at -70°C ; decomposes on heating; insoluble in water, soluble in alkalis.

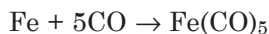
Thermochemical Properties

Iron pentacarbonyl

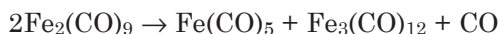
ΔH_f°	-185.0 kcal/mol
ΔG_f°	-168.6 kcal/mol
S°	80.8 cal/degree mol
C_p	57.5 cal/degree mol

Preparation

Iron pentacarbonyl may be prepared by heating iron powder at 200°C with carbon monoxide at a pressure of 200 atm.



Other carbonyls are prepared from iron pentacarbonyl. For example, iron nonacarbonyl is formed by decomposition of the pentacarbonyl when exposed to light. When nonacarbonyl in ether, benzene, or toluene is heated at 60°C, it produces dodecacarbonyl and pentacarbonyl:

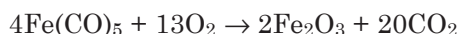
**Reactions**

Iron pentacarbonyl is stable in the dark but decomposes on exposure to light or on heating. In an alcoholic solution, the carbonyl is decomposed by acids also.

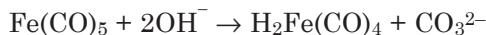
In acetic acid solution iron pentacarbonyl forms iron nonacarbonyl:



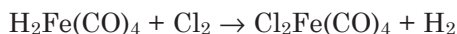
When heated in air pentacarbonyl converts to iron(III) oxide:



Reaction with an alkali produces iron hydrocarbonyl:



Iron hydrocarbonyl reacts with halogens forming halogen substituted carbonyl derivatives:



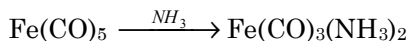
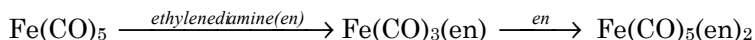
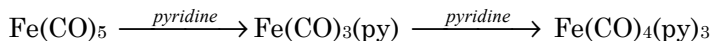
Also, iron hydrocarbonyl can combine with several metals forming metallic derivatives in which hydrogen is replaced by the metal ions:



The same product is obtained by reaction of diethylmercury with iron hydrocarbonyl:



Iron carbonyls form complexes with many donor molecules, such as pyridine, ammonia, ethylenediamine, and o-phenanthroline. In such complexes, carbonyl groups are partially replaced by the ligands. Some examples are:



Thermal decomposition of vapors yields finely divided iron powder and carbon monoxide.

Analysis

Iron carbonyls may be identified by electron diffraction and x-ray analysis. Also, its solutions in appropriate organic solvents, such as ether, methanol, or acetone may be analyzed by GC/MS. The characteristic mass spectra should indicate the molecular ions corresponding to the carbonyl as well as the mass spectra of CO and Fe(CO)_n , where n is the number of CO units in the fragmented mass ions. Flame- or furnace-AA or ICP/AES analysis may be applied on the nitric acid extract of the compound(s) after appropriate dilution to determine the concentration of iron (See Iron).

Hazard

Iron pentacarbonyl is moderately toxic by ingestion or inhalation of its vapors. LD₅₀ oral (rats): 40 mg/kg

Exposure to light evolves toxic carbon monoxide gas. The liquid is highly flammable; flash point (cc) 5°F.

IRON(II) CHLORIDE

[7758-94-3]

Formula: FeCl_2 ; MW 126.75; also forms a dihydrate, $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ [16399-77-2] and a tetrahydrate, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ [13478-10-9].

Synonyms: ferrous chloride; iron dichloride

Occurrence and Uses

Iron(II) chloride occurs in nature as the mineral lawrencite. Iron dichloride is used as a mordant for dyeing; and as a reducing agent. It also is used in pharmaceutical preparation; in sewage treatment; and in metallurgy.

Physical Properties

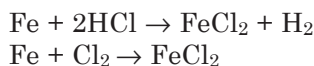
White hexagonal crystal; hygroscopic; density 3.16g/cm³; melts at 677°C; vaporizes at 1,023°C; vapor pressure 20 torr at 737°C and 200 torr at 897°C; highly soluble in water, ethanol and acetone; slightly soluble in benzene. The dihydrate and tetrahydrate are greenish monoclinic crystals; densities 2.39 and 1.39 g/cm³, respectively; decomposing at 120 and 105°C, respectively; both the hydrates soluble in water.

Thermochemical Properties

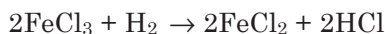
ΔH_f°	-81.69 kcal/mol
ΔG_f°	-72.25 kcal/mol
S°	28.20 cal/degree mol
C_p	18.33 cal/degree mol
ΔH_{fus}	10.28 kcal/mol

Preparation

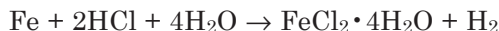
Iron(II) chloride is prepared by passing chlorine or hydrogen chloride gas over iron at red heat or 700°C:



It also may be produced by the reduction of iron(III) chloride with hydrogen or other reducing agents at elevated temperatures:



The tetrahydrate is obtained by dissolving the metal in hydrochloric acid followed by crystallization at room temperature.



The tetrahydrate gradually loses water when heated above 105°C forming dihydrate, monohydrate and the anhydrous salt. At 220°C it loses all its water of crystallization.

Analysis

Elemental composition: Fe 44.06%, Cl 55.94%. The water of crystallization in hydrate salt can be determined by gravimetry. Iron can be analyzed in the aqueous solution of the salt by AA or ICP/AES techniques (See Iron). Chloride ion can be determined by titration with silver nitrate or mercuric nitrate or by ion chromatography.

IRON(III) CHLORIDE

[7705-08-0]

Formula: FeCl_3 ; MW 162.21; occurs as a dimer Fe_2Cl_6 in vapor phase.

Synonym: ferric chloride

Occurrence and Uses

Iron(III) chloride occurs naturally as the mineral molysite. The compound is widely used to prepare a number of iron(III) salts. Also, it is applied in sewage and industrial waste treatment processes. It also is used in the manufacture of dyes, pigments and inks; as a chlorinating agent; and as a catalyst in chlorination reactions of aromatics.

Physical Properties

Dark brown hexagonal crystals; hygroscopic; density 2.898g/cm³; melts at 306°C; decomposes at 315°C; highly soluble in water (74.4g/100g water at 0°C); very soluble in alcohol, ether and acetone.

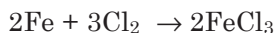
The hexahydrate is brownish-yellow crystalline mass; deliquesces; melts at 37°C; vaporizes around 280°C; highly soluble in water (92g/100g water at 20°C); very soluble in organic solvents such as ethanol, ether and acetone.

Thermochemical Properties

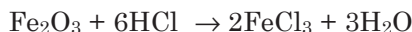
ΔH_f° (cry)	-95.48 kcal/mol
ΔH_f° (aq)	-131.5 kcal/mol
ΔH_f° (hexahydrate, cry)	-531.5 kcal/mol
ΔG_f° (cry)	-79.84 kcal/mol
ΔG_f° (aq)	-95.20 kcal/mol
S° (cry)	34.0 cal/degree mol
C_p (cry)	23.1 cal/degree mol

Preparation

Iron(III) chloride forms passing chlorine gas over iron filings at 350°C:

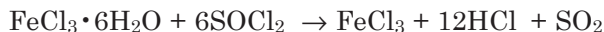


It also forms heating iron(III) oxide with HCl at elevated temperatures:



The product may be sublimed in a stream of chlorine to give high purity grade iron(III) chloride.

The anhydrous chloride also may be made by heating the hexahydrate, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, with thionyl chloride:

**Analysis**

Elemental composition: Fe 34.43%, Cl 65.57%. The compound may be identified by x-ray methods. Iron may be analyzed by various instrumental techniques (See Iron). Chloride in the aqueous solution of the compound may be measured by titrating with a standard solution of silver nitrate or mercuric nitrate or by ion chromatography.

IRON-CYANIDE COMPLEXES

Iron in both the +2 and +3 valence states forms several stable hexacoordinated octahedral complexes with cyanide (CN^-) ion, known as ferrocyanide or hexakisicyanoferrate(4-), $[\text{Fe}(\text{CN})_6]^{4-}$; and ferricyanide or hexakisicyanoferrate(3-), $[\text{Fe}(\text{CN})_6]^{3-}$, respectively. The simple iron(II) cyanide, $\text{Fe}(\text{CN})_2$ is unstable and all iron cyanide compounds known are coordination complexes.

Such cyanide complexes are also known for several other metals. All the ferrocyanide complexes may be considered as the salts of ferrocyanic acid $\text{H}_4\text{Fe}(\text{CN})_6$; and ferricyanide complexes are that of ferricyanic acid, $\text{H}_3\text{Fe}(\text{CN})_6$. The iron-cyanide complexes of alkali and alkaline-earth metals are water soluble. These metals form yellow and ruby-red salts with ferrocyanide and ferricyanide complex anions, respectively. A few of the hexacyanoferrate salts have found major commercial applications. Probably, the most important among them is ferric ferrocyanide, $\text{FeFe}(\text{CN})_6$, also known as Prussian blue. The names, formulas and the CAS registry numbers of some hexacyanoferrate complexes are given below. Prussian blue and a few other important complexes of this broad class of substances are noted briefly in the following sections:

Complex/Synonyms	Formula	CAS No.
Potassium ferrocyanide [dipotassium hexakis(cyanoferrate(4-))]	$\text{K}_4\text{Fe}(\text{CN})_6$	[14459-95-1]
Potassium ferricyanide [tripotassium hexakis(cyanoferrate(3-))]	$\text{K}_3\text{Fe}(\text{CN})_6$	[13736-66-2]
Ferric ferrocyanide[tetrairon(III) tris(hexakis(cyanoferrate))(Prussian blue)]	$\text{Fe}^{\text{III}}_4[\text{Fe}(\text{CN})_6]_3$	[14038-43-8]
Barium ferricyanide [tribarium bis(hexakis(cyanoferrate(3-)))]	$\text{Ba}_3[\text{Fe}(\text{CN})_6]_2$	[21729-04-4]
Dipotassium sodium ferricyanide [dipotassium sodium hexakis(cyanoferrate(3-))]	$\text{K}_2\text{Na}[\text{Fe}(\text{CN})_6]$	[31940-93-9]
Potassium cupric ferricyanide [potassium copper(II)hexakis(cyanoferrate(3-))]	$\text{KCu}^{\text{II}}[\text{Fe}(\text{CN})_6]$	[53295-15-1]
Potassium nickel ferricyanide [potassium nickel hexakis(cyanoferrate(3-))]	$\text{KNi}[\text{Fe}(\text{CN})_6]$	[53295-14-0]
Potassium cobalt(II) ferricyanide [potassium cobalt(II) hexakis(cyanoferrate(3-))]	$\text{KCo}^{\text{II}}[\text{Fe}(\text{CN})_6]$	[14874-73-8]
Ammonium ferrocyanide [tetraammonium hexakis(cyanoferrate(4-))]	$(\text{NH}_4)_4[\text{Fe}(\text{CN})_6]$	[14481-29-9]
Ferrocyanic acid [tetrahydrogen hexakis(cyanoferrate(4-))]	$\text{H}_4\text{Fe}(\text{CN})_6$	[17126-47-5]

Prussian blue

Prussian blue or ferric ferrocyanide or iron(III) hexakis(cyanoferrate(3-)) has the formula $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. There are several commercial applications. It is used as pigment for paints, inks, typewriter ribbons, alkyd resins, enamels,

plastics, and rubbers.

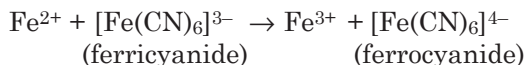
Physical properties:

Dark-blue powder or lumps; density 1.80 g/cm³; dehydrates and partially decomposes around 250°C; insoluble in water, dilute acids and most organic solvents.

Prussian blue is obtained as a dark blue precipitate by the addition of an iron(III) salt to potassium ferrocyanide solution:



A similar substance, known as Turnbull's blue, is obtained as a blue precipitate by adding an iron(II) salt to a solution of potassium ferricyanide. Iron(II) is oxidized to iron(III) by ferricyanide ion, the latter is reduced to ferrocyanide:

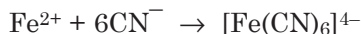


The ferrocyanide ion formed reacts with iron(III) obtained to produce Prussian blue as shown above in the reaction. Thus, Turnbull's blue is chemically the same as the Prussian blue except that it is less intense in color, probably due to the presence of a white salt of composition $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$.

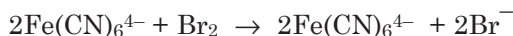
Potassium ferrocyanide

Potassium ferrocyanide, $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ occurs as a trihydrate. The compound is a spin-paired diamagnetic complex in which the ferrocyanide anion constitutes the Fe^{2+} ion, octahedrally coordinated with six CN^- ions. It is a yellow monoclinic crystalline solid; density 1.85 g/cm³; decomposes at 60°C; and soluble in water but insoluble in alcohol and ether.

The compound is obtained from the 'spent oxide' of coal gas purifiers. In the laboratory it may be prepared by treating ferrous sulfate solution with a solution of potassium cyanide:



Although ferrocyanide anion is stable at ordinary temperatures, at high temperatures it oxidizes to ferricyanide. That is, when the aqueous solution of the complex is evaporated, red crystals of ferricyanide are obtained. Similar oxidation can also occur at ambient temperatures in the presence of oxidizing agents:



Reactions with dilute acids give hydrogen cyanide:



As mentioned earlier, potassium ferrocyanide reacts with Fe^{3+} to produce Prussian blue. On the other hand, reaction with Fe^{2+} first gives a white precipitate of $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$, which can readily oxidize in the air forming Prussian blue.

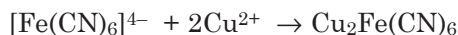
Hexacyanoferric(II) acid [$\text{H}_4\text{Fe}(\text{CN})_6$]

Hexacyanoferric(II) acid, ferrocyanic acid or tetrahydrogen hexakis(cyanate-(4-)) [17126-47-5] is used to prepare many adducts with oxygen-containing organics. Also addition compounds with inorganic salts are known. This acid may be obtained as a white precipitate upon addition of potassium ferrocyanide to concentrated hydrochloric acid:



Cupric ferrocyanide

Cupric ferrocyanide, also known as copper(II) hexacyanoferrate(II) or copper(II) hexakis(cyanoferrate(3-)) $\text{Cu}_2\text{Fe}(\text{CN})_6$, is obtained as a chocolate-brown precipitate by the addition of a copper(II) salt solution to ferrocyanide:



The above reaction also serves to determine the presence of $\text{Cu}(\text{II})$ ion in the solution.

Uses

The applications of cupric ferrocyanide are very limited. It is used as a chemical membrane for osmosis.

IRON DICYCLOPENTADIENYL

[102-54-5]

Formula: $(\text{C}_5\text{H}_5)_2\text{Fe}$ or $(\eta\text{-C}_5\text{H}_5)_2\text{Fe}$; MW 186.04; a metal π “sandwich” complex in which the six π electron system of the cyclopentadienide ion C_5H_5^- is bound to Fe^{2+} ion; $\text{Fe}-\text{C}$ distance 2.045 Å and $\text{C}-\text{C}$ bond distance 1.4 Å. Synonyms: bis(cyclopentadienyl)iron; ferrocene; dicyclopentadienyliron

Uses

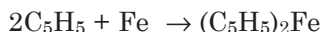
Dicyclopentadienyliron finds limited application as a catalyst. It was used earlier as an antiknock additive for gasoline. The complex also is used to synthesize other metal π -complexes and their derivatives.

Physical Properties

Orange crystals; camphor-like odor; melts at 172.5°C; vaporizes at 249°C; sublimes above 100°C; thermally stable above 500°C; insoluble in water; soluble in alcohol, ether and benzene; also soluble in dilute nitric acid and concentrated sulfuric acid forming a deep red solution that fluoresces.

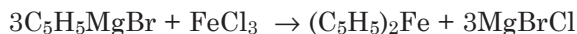
Preparation

Dicyclopentadienyliron may be obtained in a single-step synthetic route by heating cyclopentadiene with iron or iron pentacarbonyl at 300°C:

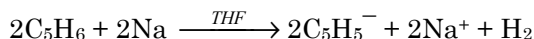


Also, it can be prepared by the reaction of iron(II) chloride with cyclopentadiene in the presence of an alkyl amine or a similar base.

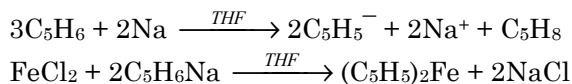
Another convenient method of preparing this π -complex of iron is a two-step process in which the first step involves preparation of cyclopentadienyl Grignard reagent, such as 2,4-cyclopentadienylmagnesium bromide $\text{C}_5\text{H}_5\text{MgBr}$ which may then be combined with ferric chloride to yield dicyclopentadienyl iron:



Another general method of preparation involves the reaction of cyclopentadiene with sodium metal or sodium hydride in tetrahydrofuran (THF). Addition of iron(II) chloride to this solution forms the complex dicyclopentadienyliron:

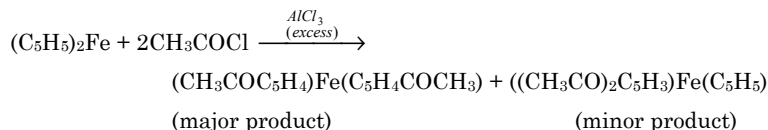
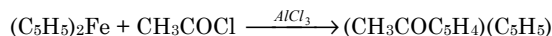


In 3:2 molar ratio of cyclopentadiene to sodium cyclopentene is obtained along with cyclopentadienide (C_5H_5^-) anion:



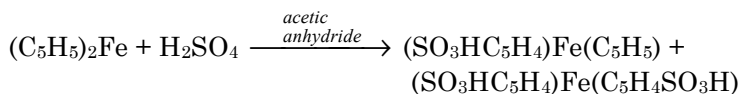
Reactions

The most important reactions of dicyclopentadienyliron may be attributed to the aromatic behavior of cyclopentadienyl ring in the complex. Thus, the ring can undergo electrophilic substitution reactions with electrophiles to form various mono-, and disubstituted products. For example, with an equimolar of acetyl chloride and in the presence of aluminum chloride, the product is essentially monoacetylferrocene; while in the presence of an excess of both of the reagents, the major product is 1,1-diacetylferrocene with a minor yield of 1,2-diacetylferrocene.

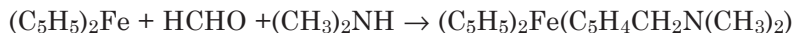


The cyclopentadienyl ring in the complex may be partially reduced by sodium amalgam in ethanol.

Reaction with sulfuric acid or chlorosulfonic acid in acetic anhydride medium gives mono- and disubstituted ferrocenesulfonic acid.



Reaction with formaldehyde in the presence of dimethylamine yields dimethylaminomethylferrocene:



The above product is an important intermediate in the synthesis of several ferrocene derivatives.

Analysis

Elemental composition: Fe 30.02%, C 64.56%, H 5.42%. An alcoholic or benzene solution of the compound may be analyzed by GC/MS. Additionally, the cyclopentadienyl ligand may be identified from the IR (303 cm^{-1}) and nmr spectra and x-ray crystallographic analysis. Furthermore, the compound may be derivatized with an electrophile (See Reactions) and the derivative formed may be identified by its physical and chemical properties and elemental composition.

IRON DISULFIDE

[1317-66-4]

Formula: FeS_2 ; MW 119.98; composed of Fe^{2+} and S_2^{2-} ions in the cubic crystals

Synonyms: ferrous disulfide; iron pyrites; marcasite.

Occurrence and Uses

Iron disulfide is found in nature in two different crystal forms, as the min-

erals iron pyrite and marcasite. The mineral pyrite is mostly used for the production of iron and sulfur. Iron disulfide also is used to produce sulfuric acid, although the latter is commercially made by other processes that are more economical.

Physical Properties

The natural pyrite consists of yellow cubic crystals; density 5.02g/cm³; hardness 6.3 Mohs; melts at 1,171°C; soluble in dilute acids.

The mineral marcasite constitutes yellow rhombic crystals; density 4.87g/cm³; transforms to more stable pyrite form when heated at 480°C; insoluble in dilute acids. Both forms dissolve in concentrated nitric acid and are insoluble in water (4.9 mg/L at 20°C).

Thermochemical Properties

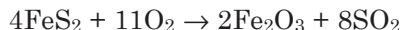
ΔH_f° (pyrite)	−42.6 kcal/mol
ΔH_f° (marcasite)	−37.0 kcal/mol
ΔG_f° (pyrite)	−39.9 kcal/mol
S° (pyrite)	12.65 cal/degree mol
C_p (pyrite)	14.86 cal/degree mol

Production

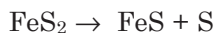
Iron disulfide is obtained from its naturally occurring minerals, pyrite and marcasite. In the laboratory it may be prepared along with iron(II) sulfide by passing dry hydrogen sulfide through a suspension of hydrated iron(III) oxide or iron(III) hydroxide in alkaline medium. The unstable product formed decomposes to FeS₂ and FeS.

Reactions

Both forms of iron disulfide are very stable at ordinary temperatures and also inert towards most chemicals. Heating at elevated temperatures gives iron(III) oxide and sulfur dioxide. This process for producing sulfur dioxide is also applied to manufacture sulfuric acid:



When the disulfide is heated at 600°C in a vacuum, it decomposes to iron(II) sulfide and sulfur:



Analysis

Elemental composition: Fe 46.55%, S 53.45%. The mineral may be characterized nondestructively by x-ray techniques. The compound may be analyzed for iron by AA or ICP/AES methods following digestion with nitric acid and appropriate dilution.